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STRONG AND SUPER-STRONG CERAMICS BASED ON ALUMINUM OXIDE AND PARTLY STABILIZED ZIRCONIUM DIOXIDE

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The authors describe the results of development of strong and superstrong ceramics based on aluminum oxide and partly stabilized zirconium dioxide using highly disperse powders and the methods of hydrostatic and hot molding and sintering in a gasostat. Ceramic materials based on aluminum oxide have strength of 300 – 750 MPa and materials based on partly stabilized zirconium dioxide have strength of 800 – 2500 MPa. These materials can be widely used in various sectors of engineering due to their high strength, wear resistance, and hardness.

Domestic and foreign manufactures widely use dense corundum ceramics in many sectors of industry, as it has a number of favorable properties needed for production: high mechanical strength hardness, wear resistance, refractoriness, thermal conductivity, and chemical resistance.

Corundum was used to develop numerous high-quality materials for electronics, electrical engineering and construction. The best known in the industry are VK-94-1, VK-100-1, TsM-332 (microlite), kartinite, minalund, sicor, coral-2 and some others. They have different microstructure, phase compositions, and properties.

Studies of the technology, properties, and service conditions of corundum products demonstrated that virtually pore-free articles with a uniform fine crystalline structure are the most suitable for the majority of application areas. Strength parameters of corundum materials, depending on the type of additives and the manufacturing methods, vary within a range of 300 – 750 MPa. Strength at a level of 700 – 750 MPa can be achieved using highly dispersed powders and sintering by means of hot compression or in a gasostat [1]. Standard sintering of industrially produced aluminum oxide varieties allows for obtaining products with bending strength of 300 – 450 MPa [2, 3].

Numerous studies have lately been focused on the development of corundum ceramics with additives of eutectic compositions of various systems and studying their effect on sintering and formation of ceramic structure and properties. A specific feature of these additives is that quantities of 0.5 – 5.0% (here and elsewhere wt.%, unless otherwise specified) have a significant effect on the specified processes. The effect of the additives is based on the formation of a small quantity of eutectic melt, which actively participates in sintering. The total porosity after sintering in this case does not exceed 2%. The melt crystallizes in cooling, therefore, ceramics with such additives does not contain a vitreous phase. One can name additives of systems $MnO – Al_2O_3 – SiO_2$, $MnO – TiO_2$, $MgO – SiO_2$, $MgO – TiO_2$, and some others, whose presence in an amount of 2 – 3% lowers the sintering temperature in air to 1300 – 1550°C. The resulting materials are dense, finely crystalline, with good properties, and bending strength of 300 – 400 MPa. Additional introduction of disperse powder of partly stabilized zirconium dioxide (PSZD) makes it possible to increase the strength of ceramics up to 550 – 600 MPa at a sintering temperature of 1450 – 1500°C.

Corundum ceramics with eutectic additives can be widely used in various fields of engineering. In addition to high strength, these materials have substantial wear resistance and good surface purity after grinding and polishing [4].

After transformation strengthening involving PSZD was discovered, solutions in the field of strong and super-strong ceramics significantly changed. Most advanced countries (approximately since 1978) began to research the technology of products based on PSZD, their properties, and application areas. Apart from PSZD, other ceramic materials of the $Al_2O_3 – ZrO_2$ system, in which zirconium dioxide exists in a tetragonal modification (stabilizer is 3 mol.% yttrium oxide) are widely used.

The bending strength of ceramics from PSZD varies in a wide range from 500 to 2500 MPa, depending on the powder production technology, molding methods, and sintering regimes. The highest values of bending strength (up to 2000 –

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2500 MPa) and crack resistance (over 15 MPa · $m^{1/2}$) have been reached in sintering products molded of ultradisperse powders by hot isostatic molding [5]. It is assumed that standard sintering can achieve strength of 800 – 1000 MPa [6].

The advantages of ceramics materials based on PSZD besides high strength and crack resistance include substantial hardness, wear resistance, a low friction coefficient in combination with metals, and a possibility of obtaining very high surface purity (R_z up to 0.01 μm). Such ceramics is used to produce various twine guides and applicators, cutting and drilling tools for treating metals and wood, medical instruments, bearings, friction couples, automobile parts, wear-resistance articles for any destination, articles of various porosity and high strength.

Strengthening of ceramics based on PSZD is based on the formation of an ultradisperse structure with a high content of the tetragonal phase, which is capable of transforming into a monoclinic phase under the effect of mechanical stresses at the apex of a crack, producing an increase in the crack volume, which results in its closing. Further evolution of the crack would require application of additional mechanical stresses, which increases the strength of articles.

Such mechanism takes place only in the case when the size of crystals after firing is significantly below 1 μm, since the tetragonal solid solution of yttrium oxide in zirconium dioxide is metastable. When the specified crystal size is exceeded, the strength of ceramics abruptly decreases due to the transformation of the tetragonal phase into a monoclinic one, i.e., a polymorphic transformation with a volume increase.

In view of the above specifics of the microstructure of PSZD ceramics, one of the most important technological stages is preparation of ultradisperse powders of tetragonal zirconium dioxide.

Researchers at the Department of Chemical Engineering of Ceramics and Refractories at the D. I. Mendeleev Russian Chemical Engineering University in early 1980-s developed a method for preparation of ultrafine PSZD powders consisting in heterophase precipitation of hydroxides from concentrated solutions of zirconium and yttrium salts into an ammonia solution.

The use of specific precipitation conditions and mechanical activation of powders allows for producing aggregates smaller than 0.1 μm consisting of particles, whose size is a few tens of nanometers. Such powders after compression in a hydrostat and sintering in a gasostat at a temperature of 1400 – 1500°C produce ceramics with bending strength up to 2500 MPa [7].

It is believed that PSZD ceramics has certain drawbacks, namely, a possible decrease in strength after protracted heating at temperatures of 250 – 350°C, especially in increased humidity due to washing out of yttrium oxide, and a decrease in strength by more than 60% at elevated temperatures (up to 1000°C).

It is possible to increase the resistance of ceramics to crystal growth in sintering and to weakening under protracted heating and to increase its hardness as well (Rockwell hardness of PSZD is about 85) by introducing about 20% ultradisperse aluminum oxide powder. Material of this composition compressed in a hydrostat and sintered in a gasostat has the highest bending strength among all types of ceramics (up to 300 MPa) and the highest crack resistance (up to 25 MPa · $m^{1/2}$), Rockwell hardness being over 90 [5].

The most widespread are ceramics with compositions close to the eutectic composition in the system Al_2O_3 – ZrO_2 containing 30% ZrO_2 in the partly stabilized state. This strong (bending strength 1200 – 1500 MPa) and viscous ceramics (crack resistance about 15 MPa · $m^{1/2}$) has been developed on the basis of ultradisperse powders prepared by heterophase precipitation from salt solutions with subsequent hot molding.

A mixture of oxides with Al_2O_3 content up to 50% subjected to hot isostatic molding (gas pressure 50 MPa, sintering temperature 1300 – 1700°C) produced ceramics with strength of 1700 – 250 MPa and the size of corundum crystal equal to 1 – 2 μm.

The bending strength of ceramic material of a eutectic composition of the Al_2O_3 – ZrO_2 system prepared by standard sintering reaches 1000 MPa, furthermore, ceramic becomes denser, has finer crystals, and is stronger when sintered in vacuum compared to sintering in air.

All these ceramics with unique properties significantly increase the quality of new engineering products made from them.

A promising material for wear-resistant high-temperature products is strong ceramics based on a eutectic composition of the system Al_2O_3 – ZrO_2 – Y_2O_3, which in synthesis produces zirconium dioxide in the form of a cubic solid solution. The latter is responsible for the absence of a polymorphic transformation, which makes it possible to preserve strength properties up to a temperatures above 1200 – 1300°C, and ensures hardness and wear resistance. Such materials were developed due to the method of heterophase precipitation of powders and the development of a fine-crystalline structure in ceramics after sintering, with the grain size equal to a fraction of a micrometer and a uniform distribution of components. Hydrostatic molding of samples from these powders at a pressure of 200 – 500 MPa makes it possible to reach bending strength up to 1000 MPa using traditional sintering in vacuum. Accordingly, hot molding or gasostatic sintering can raise the strength of ceramics 1.5 – 2 times [8].

All considered compositions can be used to produce strong porous ceramics with pores sizes ranging from micrometers to millimeters depending on the production method, which is currently widely used for filtration of various gases and liquids. Materials produced from PSZD have porosity around 50%, pore size below 1 μm, strength up to 200 MPa after sintering in an air medium at 1000 – 1200°C.

The use of intensely sintering alumina makes it possible to produce strong porous materials (with porosity up to 40 – 50%) and articles with high chemical resistance for various filtering systems. Highly disperse powders based on partly stabilized zirconium dioxide and aluminum oxide are successfully used for developing a selective layer on filter elements [9] and in products for construction.

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